July 1890

On the Determination of Specific Heat and of Latent Heat of Vaporization with the Vapor Calorimeter

Harold N. Allen
University of Nebraska - Lincoln

UNIVERSITY STUDIES.

VOL. I. *JULY, 1890.* NO. 3.

I.—*On the Determination of Specific Heat and of Latent Heat of Vaporization with the Vapor Calorimeter.*

BY HAROLD N. ALLEN.

INTRODUCTION.

JOLY,[1] in 1886, and Bunsen,[2] shortly afterwards, described two similar pieces of apparatus intended to determine the specific heat of substances by means of the condensation of water vapor upon them. The name given by Bunsen to this apparatus and adopted here is *vapor calorimeter.* Bunsen also intended his instrument to be used in the determination of the latent heat of vaporization of various liquids, and it is the object of the present paper to describe experiments testing the steam or vapor calorimeter in this direction. A rough experimental instrument was first constructed, combining to a certain extent the principles of Joly and of Bunsen, and this proving fairly satisfactory, an apparatus was made by a local tinman, which, while much less expensive than Joly's final form, worked in a very satisfactory manner.

A number of determinations of *specific heat* were made with both instruments, to which however no further im-

[1] J. Joly (Dublin), Proc. Roy. Soc., Nov. 1886.
[2] R. Bunsen, Wied. Ann. d. Chem. u. d. Phys., Band XXXI., 1887.

portance is to be attached than as showing the short time needed for heating the body experimented on to 100° C., and the very slow rate at which the weight of the substance and condensed water changes after that time. Experiments on the latent heat of evaporation of alcohol remained without definite result owing to water contained in it, but a certain amount of success was obtained with bisulphide of carbon, though here too the same difficulty was encountered.

I have to thank Professor F. Kohlrausch, Director of the Physical Institute in Strassburg, for the great help given in the course of these experiments, and the kindness he has uniformly shown me.

THEORY OF THE METHOD.

Suppose that a number of substances, with weights W_1, W_2, W_3, etc., and specific heats S_1, S_2, S_3, etc., and with the common temperature $t°$, are plunged into the saturated vapor of a liquid, the latent heat of vaporization of which is λ, and the temperature T. Then a certain weight w of the liquid will be condensed such that the heat given up in condensation is equal to that required to raise the temperature of all the bodies from $t°$ to $T°$.

$$W\lambda = (W_1S_1 + W_2S_2 + W_3S_3 + \text{etc.})\ (T - t).$$

This affords a means of determining the specific heat of one of the bodies if the specific heats of the others and the latent heat λ are known, or of finding λ if the specific heats are known. The great difficulty is in the determination of w,—the weight of the condensed liquid,—as a removal of the substances from the vapor causes in general instant evaporation.

Both Bunsen and Joly adopt the expedient of weighing the whole suspended in steam, the difference between the methods being that while Bunsen plunges substance and carrier into a vessel of steam, Joly surrounds them with steam as quickly as possible by suddenly passing it into the vessel in which they hang.

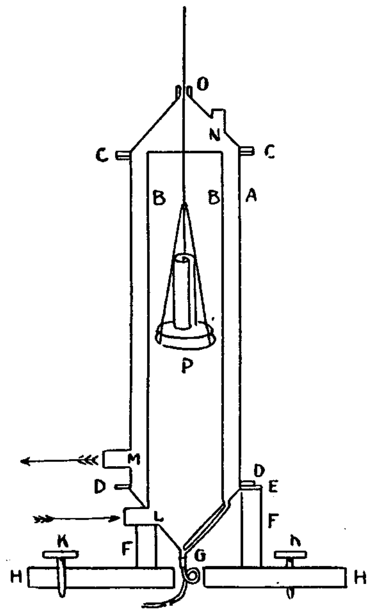

FIG. 1.

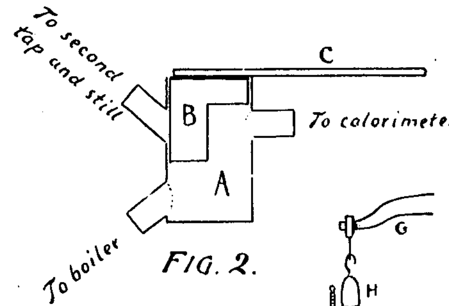

FIG. 2.

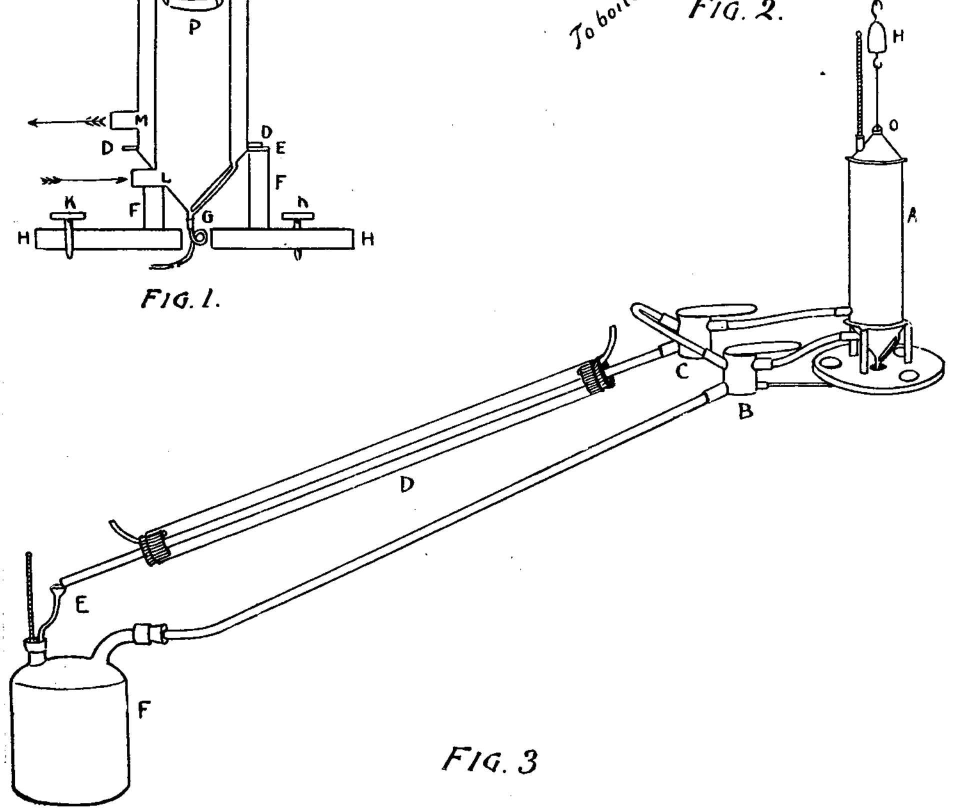

FIG. 3

DESCRIPTION OF APPARATUS.

The final apparatus used was constructed as follows: AA (Fig. 1) is a cylinder of sheet brass, seven centimeters in diameter and twenty-two in height. At the bottom of this is soldered the ring D, turned out of sheet brass, to which a cone of thin brass is fixed, carrying the tubulure L, the small pipes G, and the inner cylinder of thin brass BB. At the top of A is soldered the lower one of two flat rings of brass C, which are ground together and held in contact by means of a bayonet joint. To the upper of these rings is soldered a brass cone bearing the tubulures N and O. To the ring D are soldered three brass ears E, to which the wooden pillars F are screwed. These are fixed to the round wooden base H provided with levelling-screws K.

The tubulure O is filled with plaster of paris, through which a vertical hole of about two millimeters' diameter is bored. A fine platinum wire, suspended from a lead counterpoise, which takes the place of one scale-pan of a balance, passes through this hole and carries at its lower end the body to be experimented on. Under this hangs a small cup of platinum or brass to collect the condensed liquid. In some cases two of these are used, one underneath the other, to catch any possible droppings.

The instrument in this form is not quite as convenient as the second one described by Joly, but its construction is much easier, and it is probably lighter, and therefore more quickly heated by the steam. It is much higher than is necessary for ordinary purposes, having been designed for a special use. If the cylinder A were half its actual length, the apparatus would be much more compact and would probably work better.

Figure 3 shows the complete apparatus with arrangements for passing any desired quantity of vapor through the calorimeter and returning the condensed vapor to the boiler.

From the boiler F the vapor passes to the tap B, the construction of which is shown in Figure 2. It consists of a short piece of wide brass tubing A, the lower end being closed by a brass disc, while short brass tubulures are soldered over three holes in the sides. B is a piece of brass tubing ground into A, and having one-half of the lower part cut away as shown. The top is closed by a brass disc, to which the handle C is fixed.

It will be seen that in the position indicated there is free communication between the boiler and calorimeter in the tap B, and between the calorimeter and still in C, which is constructed on exactly the same plan. If both taps are turned through 180°, the vapor passes direct from B to C, and so to the still, while by turning through a less angle part can be made to pass through the calorimeter, the rest going directly to the still. In this way the former amount can be regulated.

METHOD OF DETERMINING SPECIFIC HEAT.

The order of an experiment was as follows: —

The upper cone was removed, the wire passed through the small hole in the plaster of paris, the carrier and substance P hooked on, the cone set in place on the instrument, and the upper end of the wire hooked to the arm of the balance. During this operation the wire was kept from rubbing against the plaster by means of two small pieces of brass, which filled the hole, leaving room for the wire in grooves on the surfaces where they met. The balance, the pillar of which was mounted on a tripod with levelling-screws, was then shifted until the wire hung in the centre of the hole; the two halves of a wooden case surrounding the calorimeter were pushed together, openings being left for the wire, the thermometer, the steam pipe, and the escape pipe. The instrument was then left for a long time (best over night) to take a uniform temperature.

The weight of substance and carrier in air having been determined, and the thermometer in N read, removed, and replaced by a cork, steam was admitted suddenly at L by thrusting into the tubulure a tight-fitting brass tube, connected by means of rubber tubing with a steam boiler. The steam passed up through B, down between B and A, and out through M. After the first minute the flow of steam was slackened so that very little came out either at M or O.

In the first experiments M was connected with a long glass tube, which carried the waste steam to some distance from the instrument and balance. The steam or vapor escaping through O was removed by the method adopted by Bunsen; a tube was set with its opening at right angles to O, and led to an iron chimney in which a gas flame was kept burning. In this way an air current was formed, which prevented anything from rising to condense on the balance above. After about five minutes the weight of the carrier and substance with the water condensed was determined, and this was repeated at intervals of five minutes for some time.

It was found that with a good conducting substance the weight found at the end of ten minutes could be taken as correct, as after this there was little increase, and that probably due to condensation on the suspending wire.

The regulation of the flow of steam was attended with some difficulty: the least irregularity caused in the end an increase of weight. Where the regulation was attempted, as at first, by turning down the flame under the boiler, the blowing aside of the small flame during a few seconds spoiled several experiments.

With the complete apparatus, provided with taps and condenser, this difficulty was not felt, as the gas was full on the whole time.

RESULTS.

The following are the results obtained with the first large tinned iron instrument:—

SPECIFIC HEAT OF BRASS AND IRON.

MATERIAL.	WEIGHT.	RESULT.
Brass	105 grm.	$S = 0.0922$
Brass	105 grm.	$S = 0.0938$
Brass	105 grm.	$S = 0.0932$
Iron	123.05 grm.	$S = 0.1144$
Iron	123.05 grm.	$S = 0.1148$

LATENT HEAT OF VAPORIZATION OF ALCOHOL.

MATERIAL.	WEIGHT.	RESULT.
Brass in alc. vapor	135.33	$\lambda = 252$
Brass in alc. vapor	46.43	$\lambda = 232$

The following results were obtained with the smaller brass apparatus:—

SPECIFIC HEATS.

MATERIAL.	WEIGHT.	RESULT.
Copper	40.28	$S = 0.093$
Copper	40.28	$S = 0.091$
Quartz	28.68	$S = 0.1894$
Quartz	28.68	$S = 0.1933$
Quartz	28.68	$S = 0.1902$
Quartz	28.68	$S = 0.1929$
* Quartz	28.68	$S = 0.1902$
* Quartz	28.68	$S = 0.1908$
Platinum	23.95	$S = 0.0315$

In the two experiments with quartz marked * a very fine platinum wire was used for suspension in place of the coarser one used before, and it was found that this had a very large influence on the constancy of the balance. In the determination of the specific heat of platinum it was found that the quantity taken was not enough to give an accurate result. The specific heat of platinum is so low that the quantity of water condensed was small.

LATENT HEAT OF VAPORIZATION OF ALCOHOL.

MATERIAL.	WEIGHT.	RESULT.
Copper in alcohol	45	$\lambda = 656.4$
Copper in alcohol	45	$\lambda = 387$
Platinum in alcohol	40	$\lambda = 610$

These curious results seem to be due to varying amounts of water mixed with the alcohol used. In the first case λ is actually greater than in the case of water vapor. It is, however, possible that some of the condensed alcohol may have dropped off, though this is hardly likely in the last case where the quantity condensed was small. This substance was not further investigated.

LATENT HEAT OF VAPORIZATION OF CARBON BISULPHIDE.

A large number of experiments were made with this compound, several different bodies being tried to condense the vapor. The best results were obtained with a plate of nickel, weighing 24.10 grams, which was rolled into a spiral and suspended over the lid of a platinum crucible, a shallow cup of platinum foil being hung beneath this. The whole weight of platinum was 6.98. This combination under the circumstances of the experiments condensed more than 0.8 grams of carbon bisulphide.

In an experiment made July 29, 1889, the initial temperature of the calorimeter was 18.9, while the temperature after the admission of vapor was 46.4. The thermometer used was compared with a standard thermometer which had been corrected at the Reichs-institut.

The apparent increase of weight was 0.929 grams, and to this must be added a correction of 0.0083 grams due to reduction of the weights to vacuo.

The equation

$$(W_1S_1 + W_2S_2)\ (T - t) = w\lambda$$

becomes

$$(24.10 + 0.10916 + 6.98 \times 0.0323)\ 27.5 = 0.9373\lambda,$$

the number 0.10916 (Regnault) being taken as the specific heat of nickel, and 0.0323 (Violle) as that of platinum. Thus this experiment gives

$$\lambda = 83.79.$$

The following is a list of all the successful experiments made with the spirally rolled nickel, two being left out which failed on account of the gradual increase of impurity in the carbon bisulphide, and one in which the draught was not at work. The carbon bisulphide used in the last three experiments was carefully freed from water by distillation over phosphorous pentoxide. Admixture of water or of some other impurity, perhaps sulphur, seems to lower the latent heat, a value as low as 76 having been obtained with impure substance.

w.	$T-t$.	λ.
0.8752	26.05	85.0
0.8386	25.05	85.30
0.8341	24.6	84.22
0.9143	27.0	84.33
0.9814	28.65	83.36
0.9373	27.5	83.79
		Mean, 84.33

CORRECTION TO VACUUM.

Let n be the true weight of the nickel,
" p " " " " " platinum,
" c " " " " " carbon bisulphide.

The volume of the nickel and platinum at the air temperature may be taken as

$$\frac{24}{8.9}+\frac{6.98}{21.5}=3.03 \text{ cc.};$$

that of the brass weights as

$$\frac{31.06}{8.4}=3.69 \text{ cc.}$$

The actual weight of the nickel and platinum is therefore

$$n+p=31.06-(3.69-3.03)\,0.001213,$$

0.001213 being the density of air at mean temperature and normal pressure. The volume of the nickel and platinum at 46° has been assumed as 3.33 cc., that of 0.929 grams of CS_2 is 0.76 cc., if the density is calculated from Hirn's formula for the expansion of this liquid. The volume of the platinum weights added in the other scale-pan is 0.04 cc.

Thus on one side the nickel, platinum, and carbon bisulphide displace 4.07 cc. of carbon bisulphide vapor, while on the other $3.69 + 0.04$ cc. of air are displaced.

Then

$$n + p + c + 4.07 \times 0.00296 = 31.06 + 0.929 + (3.69 + 0.04)\ 0.001213.$$

$$\text{Thus } c = 0.929 + 3.73 \times 0.001213 + 0.66 \times 0.001213 - 4.07 \times 0.00296$$
$$= 0.9373 \text{ grams.}$$

The number 0.00296 for the density of carbon bisulphide vapor is obtained by substituting, in Clausius' equation for the density of saturated vapors, the values found by Joule and Regnault for E and $\frac{dp}{dT}$.

In conclusion it may be remarked that the method is only available in the case of a few vapors, on account of the large amount of substance used up in the determinations.